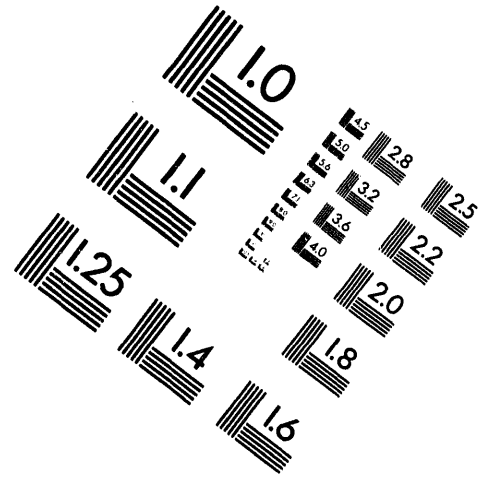


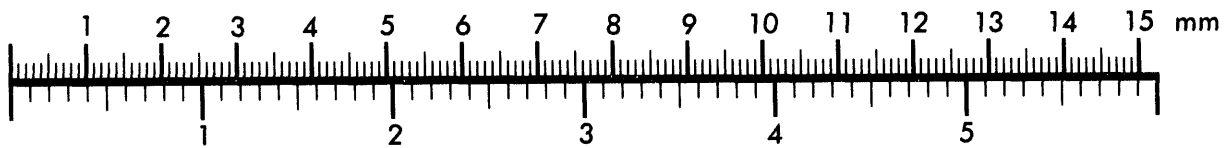
AIM

Association for Information and Image Management

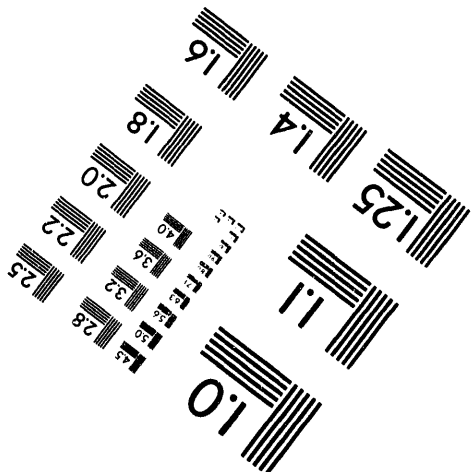
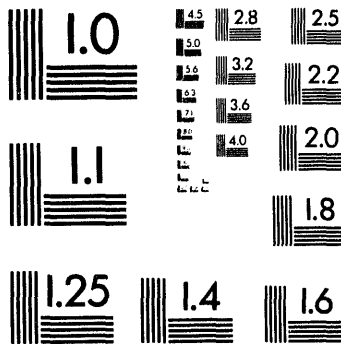
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202



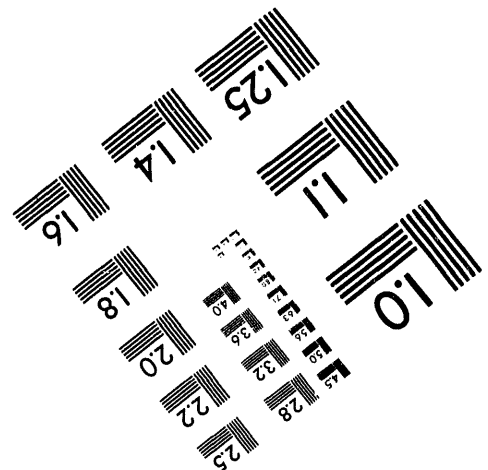
Centimeter



Inches



MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.



1 of 1

SECOND QUARTERLY REPORT

U. S. DEPARTMENT OF ENERGY

SURFACTANT DEVELOPMENT FOR ENHANCED OIL RECOVERY

GRANT NO. DE-FG22-93MT93007

Prepared By

**The Morgan State University
Fossil Energy Consortium**

May 17, 1994

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Se

SURFACTANT DEVELOPMENT FOR ENHANCED OIL RECOVERY

SECOND QUARTERLY REPORT

This report covers the period from January 1, 1994 to March 31, 1994. It summarizes the activities of the grant during this period to develop novel surfactants for enhanced oil recovery, and represents the second quarterly report.

MEETINGS OF THE CONSORTIUM MEMBERS

During the second quarter of the project, there have been no formal meetings between the consortium members. However, there has been constant communication by telephone and correspondence between the members to discuss programmatic and administrative aspects of the project. Some of the informal programmatic discussions have concentrated on the directions to take for synthesizing and screening new surfactants.

OVERVIEW OF WORK PERFORMED DURING PERIOD

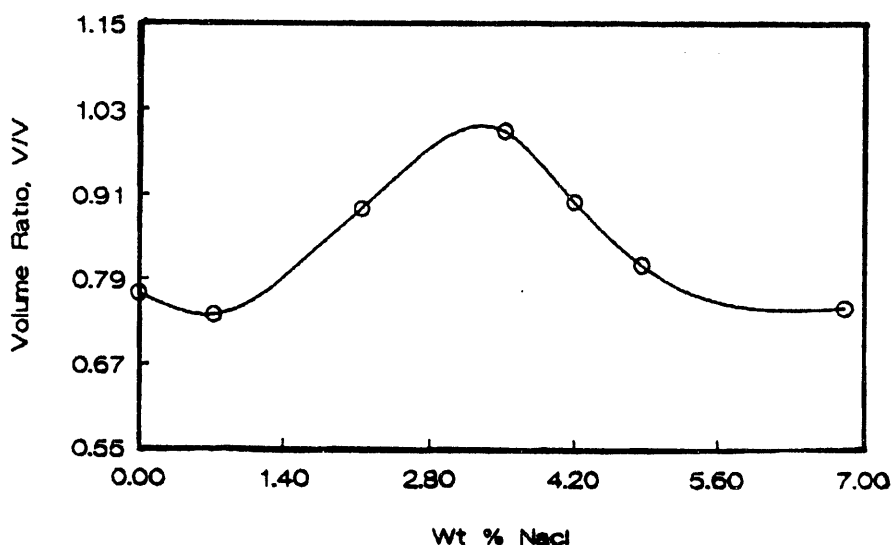
During the period covered by this report, several research activities both from the synthetic point of view and characterization of surfactants were performed. Of immediate interest was the investigation of surfactants identified in the first quarterly report, such as cetyltripropylammonium bromide and cetyltributylammonium bromide. Interest was generated about these surfactants because of the low critical micelle concentration they exhibited. Salinity tests and influence of surfactant concentration on the uptake of oil by the aqueous solutions of these surfactants were investigated at Morgan State University. South Carolina State University has been investigating the highly branched homologues of these surfactants and the *Institute for College Research Development and Support* has provided extensive administrative and management support to the project.

SPECIFIC TASKS COMPLETED

- (1) ***CONDUCT OF LECTURES:*** Formal lectures on surfactant chemistry are continuing to be made to students at Morgan State, so that they might ultimately achieve proficiency in the field of colloid and surfactant technology.
- (2) ***USE OF THE COMPUTATIONAL METHOD:*** A method for obtaining micellar diffusion coefficients from conductivity data was carried out and the obtained result will be presented at the Mid Atlantic Regional Section meeting of the American Chemical Society, to be held in Baltimore, Maryland, May 25 through May 26, 1994. The surfactants studied for this presentation are those containing the benzyl group as the surfactant headgroup. This class of surfactants was discussed in the previous quarterly report. The method used involved obtaining transport numbers, individual ionic conductances, and the micellar electrophoretic effect. These parameters were combined to calculate the diffusion coefficient for cetyltrimethylammonium bromide as a reference point. The diffusion coefficient, D , for the other surfactants were similarly obtained. The D values obtained are 1.02×10^{-6} and $1.5 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively.
- (3) ***CHARACTERIZATION OF SURFACTANTS***
 - (a) ***Conducting Salinity Tests:*** A salinity test, for cetyltripropylammonium bromide (CPAB) was conducted, which involved the influence of an electrolyte on the uptake of oil. A known weight percent of sodium chloride (NaCl) was added to a mixture containing equal volumes of solvents, water and hexane (4.0 ml). Ten replicate samples containing different weight percents of sodium chloride were then prepared. Each of these mixtures also contains 0.20 g. of surfactant. The mixtures were then sonicated for two minutes using ultra sonication for quick dissolution of the solids. They were subsequently stirred vigorously with a stirring bar

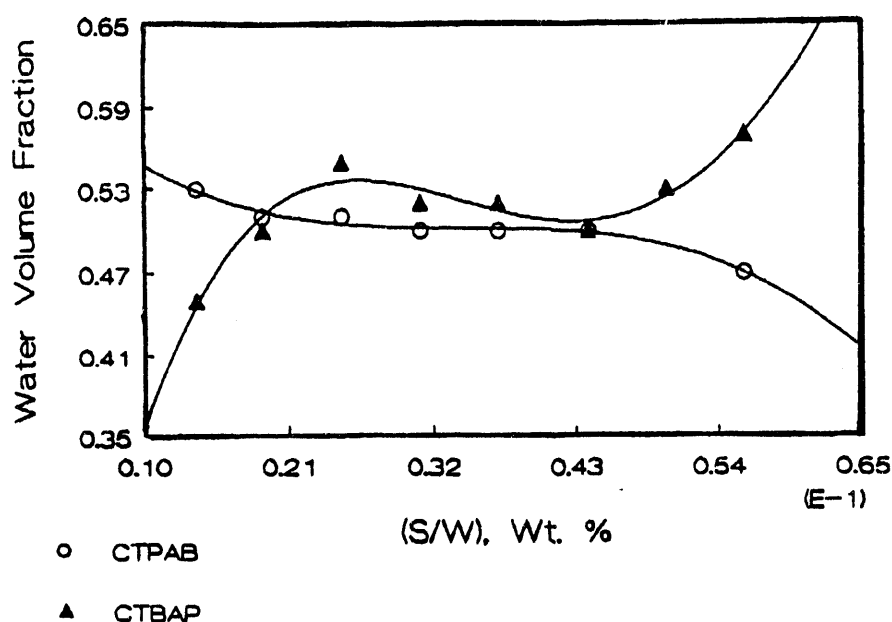
for about 30 minutes. The mixture was then allowed to stand for twenty four hours to allow for equilibration. Upon attainment of equilibrium, most of the systems were observed to consist of three phases: (1) a water-rich phase, (2) a surfactant-rich phase and (3) an oil-rich (hexane) phase. The volume of each phase was carefully measured. Figure 1 shows the data obtained from this experiment. As can be seen, a maximum at sodium chloride weight percent of 2.89 has been obtained. The volume ratio of oil to water at this point was 1.0. This is the point usually taken as the optimum salinity. At this point, the interfacial/surface tension is at the minimum and the surface tension reduction ability of the surfactant is at the maximum, a critical criterion for enhanced oil recovery. Due to instrument difficulties, surface tension/interfacial tension measurement could not be made to establish the actual surface tension value. This will be discussed in the next quarterly report. From this measurement it is believed that CPAB and some of its derivatives, may hold promise, and could be one of the surfactants that will be investigated further, as related to other additives.

FIGURE 1
SALINITY CURVE FOR CETYLTRIPROPYLAMMONIUM BROMIDE



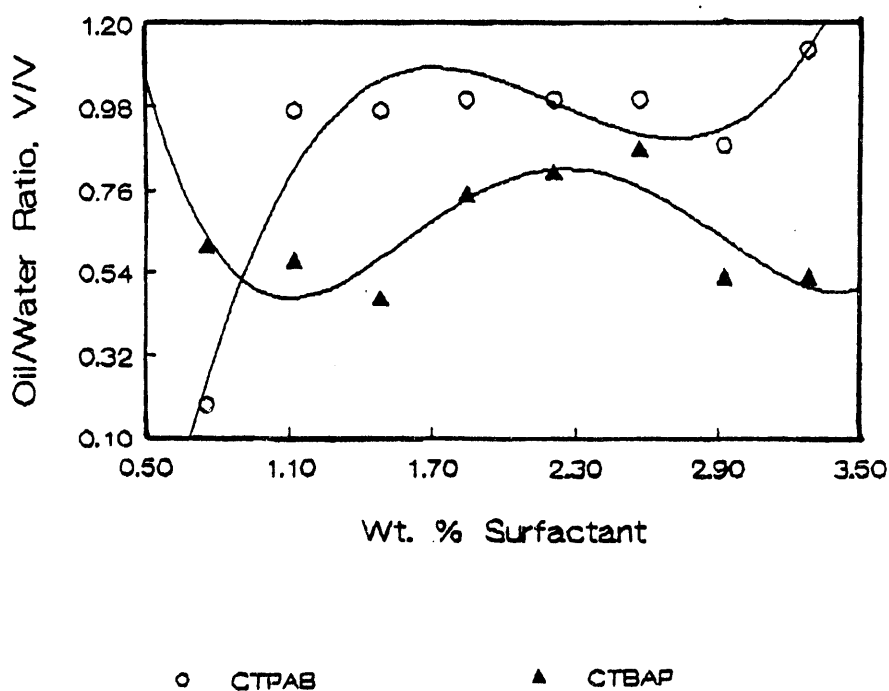
(b) *Solubilization:* The uptake of oil and or water using cetyltripropylammonium bromide and cetyltributylammonium bromide (CTBAB) was conducted by adding different amounts of these surfactants to equal volumes of oil and water. Eight samples were prepared for each surfactant as described above, except in this experiment, no electrolyte was added. The volumes of oil and water for each compound were kept constant at 8.0 ml. In each case two phases were obtained, except in the case of the tripropyl group in which there were three phases at the lowest surfactant concentration. Further observation of the systems show that most of the surfactant was dissolved in the oil phase as in the case of the cetyltripropylammonium bromide where the surfactant was dissolved almost equally between the two phases at low surfactant concentration. In fact, at the surfactant weight percent of 1.5, the meniscus between the phases is so barely visible, that the system could pass as one continuous phase. Beyond this point, the surfactant solubility becomes more apparent in the organic phase than in the aqueous phase. Figure 2 shows water

FIGURE 2
SOLUBILIZATION CURVE:
(S/W) WEIGHT PERCENT VS. WATER VOLUME FRACTION



volume fraction for the two surfactant systems as a function of surfactant to water ratio (S/W). As can be seen from this figure there is a region of phase inversion for each system. For the propyl group, there seems to be an oil uptake of surfactant into the aqueous phase. This uptake decreased very gradually until about the point of S/W 0.043, when the uptake drops more rapidly. For the butyl group a phase inversion occurred at this same point, except in this case the uptake is into the aqueous phase. This trend was also manifested when the oil/water ratio was plotted against the weight percent of surfactant as can be seen in Figure 3. It will be interesting to note that the point at which these phase inversions occur coincide with the point at which optimum salinity was observed in Figure 1 (the same weight percent surfactant as the electrolyte weight percent).

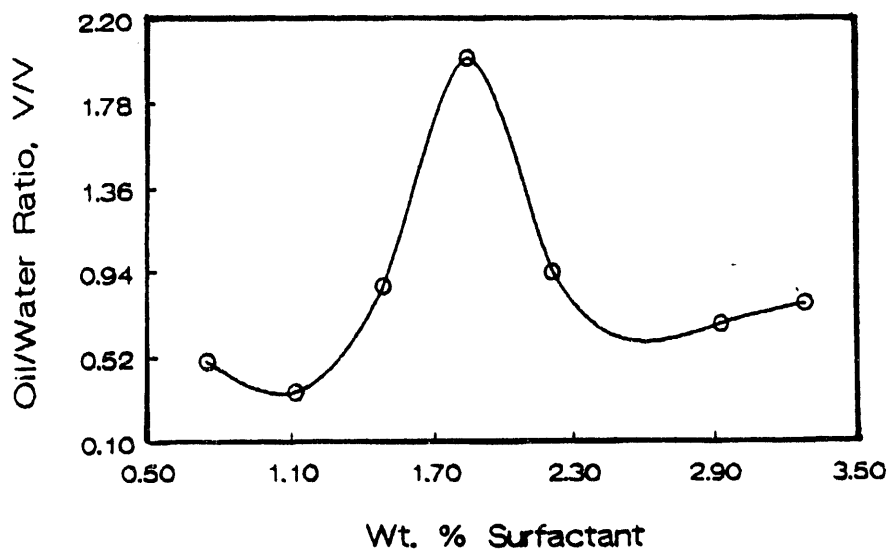
FIGURE 3
SOLUBILIZATION CURVE:
OIL WATER VOLUME RATIO VS. WEIGHT PERCENT OF SURFACTANT



The interesting phase characteristics exhibited by these surfactants will make these surfactants and their analogues candidates for further screening. It is strongly believed that these effects are as a result of the bulky headgroup that these surfactants possess.

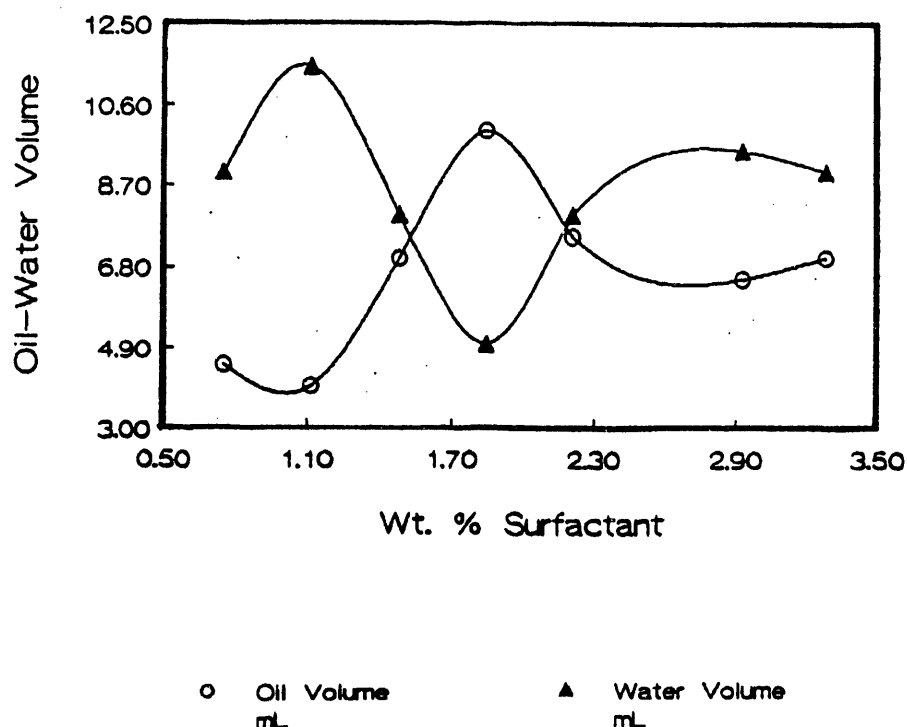
- (c) *Solubilization of Didodecyldimethylyammonium bromide (DDAB):* This double-tailed compound is a class of surfactants which is of interest because of their extraordinary ability to form bicontinuous microemulsions and solubilize large quantities of polar and non-polar solutes. Samples for solubilization studies were prepared and analyzed exactly as described for CPAB and CTBAB. Unlike the single-chain surfactants, DDAB is mainly solubilized in the aqueous phase. There was observed an initial gradual increase in the uptake of water-surfactant into the oil phase. Also observed was a surfactant weight percent of 1.85, a maximum in the oil/water ratio. At this point, and only at this point, was the surfactant

FIGURE 4
SOLUBILIZATION CURVE FOR DDAB:
OIL-WATER VOLUME RATIO VS. WEIGHT PERCENT OF SURFACTANT



seen to be in the oil phase. However, beyond this point of 1.85, the surfactant reverts to the earlier observed trend. This phase behavior is shown in Figure 4. When the different volumes of water and oil were plotted as a function of surfactant weight percent the maximum attainment exhibited in Figure 4 was also apparent. At the oil volume maximum, as illustrated in Figure 5, the water volume showed a minimum but increased thereafter, as the oil phase continued to decrease. This volume decrease is due to the uptake of oil into the water-surfactant rich phase. Thus, the surfactant DDAB and its longer chain homologues, will receive extensive screening throughout the project period.

FIGURE 5
SOLUBILIZATION CURVE FOR DDAB:
OIL-WATER VOLUME VS. WEIGHT PERCENT OF SURFACTANT



FUTURE WORK

The project activities for the next quarterly report will concentrate on the progress made in the synthesis of longer chain (C-16) double tailed surfactants, together with very highly branched surfactants. Characterization of these surfactants and further evaluation of the surfactants studied in this second quarterly report will involve the use of spectroscopic, surface, and interfacial surface tension techniques.

DATE

FILMED

10 / 5 / 94

END

